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(54) Title: DETERGENT BLEACH COMPOSITION

(57) Abstract

Concentrated detergent powder compositions are disclosed having a bulk density of above 600 g/l, and comprising a surfactant, a detergency builder, a peroxy bleach compound, and a specific type of dinuclear manganese complex as effective bleach catalyst. A particularly preferred dinuclear manganese complex is: $[(Et\text{-bridged}(Me_2TACN)_2)Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)]^{2+}(PF_6^-)_2$. Said bleach catalyst was found to exhibit favourable storage stability in a concentrated detergent powder composition according to the invention.

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Detergent Bleach Composition

Field of the invention

This invention relates to concentrated detergent powder compositions. More particularly, the invention relates to improved, concentrated and highly concentrated, also called super-concentrated, heavy duty laundry detergent bleach powder compositions.

Background of the invention

Recently, considerable interest has been shown within the detergent industry as well as among consumers and sale centres in concentrated to highly concentrated detergent powder compositions having a relatively high bulk density of above 600 g/l. The term "detergent powder composition" used herein refers to particulate detergent compositions consisting of granules or particles or mixtures thereof, of a size which, as a whole, will have the appearance of a powdered composition. Currently, highly concentrated detergent powder compositions having a bulk density of at least 650 g/l to even above 750 g/l have been commercialised.

The advantages of concentrated detergent powder compositions are evident, of which the following are particularly worth mentioning:

(i) smaller containers or packs provide easier handling to the consumer;

(ii) savings in storage and transport costs;

(iii) smaller packs create shelf space for stacking more pack per unit space;

(iv) less packing material .

For the concentration of powdered detergents and to achieve smaller packs, in priciple the following possibilities exist:

- using more activ components;

- av iding activity losses during th manufacture and storage;
- minimizing the amount of or avoiding all non-functional ingredients used in the manufacturing process;
- minimizing the amount of air and moisture in the product as well as in the packet.

Non-functional ingredients are ingredients not really essential to the washing performance; an example of such ingredient is sodium sulphate. Minimizing the amount of air in the product and packet can be achieved by densifying and shaping the particles so as to reduce the specific volume of the product, i.e. increasing the bulk density.

Essential ingredients in the formulation of modern heavy duty detergent compositions are bleaching agents for the removal of bleachable stains.
The bleach system as generally used in concentrated and highly concentrated detergent powder formulations consists of a mixture of a peroxygen bleach compound, e.g. sodium perborate mono- or tetrahydrate, particularly the monohydrate, or sodium percarbonate, and a peroxyacid bleach precursor, e.g. tetraacetylethylene diamine (TAED).

Normally, the required level of sodium perborate or other peroxygen compound in such compositions will be from about 10 to 25% by weight, and the peroxyacid bleach precursor, e.g. TAED, is generally present at a level of from 2 to 10% by weight, making up to a total level of bleach system of from about 12 to 35% by weight of the composition.

EP-A-509,787 discloses a concentrated detergent powder formulation comprising a surfactant, a detergency builder, a peroxygen bleach compound, and additionally a triazacyclon nan -based manganese complex bleach catalyst. In contrast to peroxyacid bleach precursors, which function

by the mechanism of reacting with the peroxygen compound forming the corresponding peroxyacid, the bleach catalysts disclosed by EP-A-509,787 work differently and are effective already in very small amounts.

In several patent documents, for instance EP-A-458,397 and EP-A-458,398, these triazacyclononane-based manganese complexes are disclosed, which display a very high catalytic oxidation activity at low temperatures, and which are, therefore, particularly suitable as bleach catalysts. A major improvement of the bleaching activity could be obtained by the fact that these compounds are more stable under washing conditions e.g. oxidising environment (as a result of the presence of hydrogen peroxide or peroxyacids).
However, we found that the storage stability of these manganese complex bleach catalysts in concentrated detergent powders nevertheless leaves room for improvement.

In EP-A-544,490, a specific group of manganese complexes is disclosed which comprise two ligand of formula

$$\left[NR^3 - (CR^1(R^2)_u)_t \right]_s$$

wherein t is an integer from 2 to 3;
s is an integer from 3 to 4;
u is zero or one;
R^1 and R^2 are each independently selected from H, alkyl, aryl, both optionally substituted; and
R^3 is independently selected from hydrogen, alkyl, aryl both optionally substituted, with the proviso that a bridging unit R^4 is formed by one R^3 unit from each ligand where R^4 is the group $C_nR^5R^6-(D)_p-C_mR^5R^6$ where p is zero or one;
D is selected fr m a heteroatom such as oxygen and NR^7 or is part of an aromatic or saturat d hom nuclear r

heteronucl ar ring;

n is an integer from 1 to 4;

m is an integer from 1 to 4;

with the proviso that n + m <= 4 if p is zero or p is one and D is part of an aromatic or saturated homonuclear or heteronuclear ring; and that n + m <= 3 if p is one and D is a heteroatom such as oxygen or NR^7;

R^5 and R^6 are each independently selected from H, NR^8 and OR^9, alkyl, aryl, optionally substituted and R^7, R^8 and R^9 are each independently selected from H, alkyl, aryl, both optionally substituted.

We have now surprisingly found that the storage stability of the above-identified specific group of manganese complexes disclosed by EP-A-544,490 present in concentrated detergent powders is considerably improved as compared to the storage stability of the manganese complex catalysts disclosed by EP-A-458,397 and EP-A- 458,398, even at higher levels of the bleach system than normally used.

<u>Definition of the invention</u>

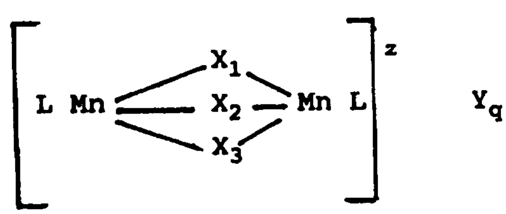
The present invention relates to a concentrated detergent powder composition having a bulk density of above 600 g/l, comprising:

(a) from 10 to 50% by weight of a surface active material;

(b) from 15 to 80% by weight of a detergency builder or builder mixture;

(c) from 5 to 35% by weight of a peroxy bleaching agent; and

(d) from 0.004 to 1.0 by weight of a bleach catalyst, characterised in that said bleach catalyst is a dinuclear manganese complex having the formula:



wherein Mn is manganese which can individually be in the III or IV oxidation state; X_1, X_2 and X_3 each independently represent a coordinating or bridging species selected from the group consisting of H_2O, O_2^{2-}, O^{2-}, OH^-, HO_2^-, SH^-, S^{2-}, >SO, Cl^-, N_3^-, SCN^-, $RCOO^-$, RSO^-_3, RBO_2^{2-}, NH_2^- and NR_3, with R being H, alkyl, aryl, both optionally substituted, $R'COO^-$ where R' is alkyl, aryl, both optionally substituted; L is a ligand which is an organic molecule containing at least three nitrogen atoms which coordinates via all or some of the nitrogen atoms to the manganese centres; z denotes the charge of the complex and is an integer which can be positive or negative; Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the charge z of the complex; and q = z/[charge Y]

whereby the bleach catalyst comprises two ligands L having the formula:

$$\boxed{\left[NR^3 - (CR^1(R^2))_t\right]_s}$$

wherein t is an integer from 2 to 3; s is an integer from 3 to 4; R^1 and R^2 are each independently selected from H, alkyl, aryl, both optionally substituted; and R^3 is independently selected from hydrogen, alkyl, aryl both optionally substituted, with the proviso that a bridging unit R^4 is formed by one R^3 unit from each ligand where R^4 is the group $C_nR^5R^6-(D)_p-C_mR^5R^6$ where p is zero or one; D is selected from a heteroatom or a heteroatom containing group, such as oxygen and NR^7, or is part of an aromatic r saturated homonuclear or heter nuclear ring; n is an integer from 1 to 4;

m is an integer from 1 t 4;
with the proviso that $n + m \leq 4$;
R^5 and R^6 are each independently selected from H, NR^8 and OR^9, alkyl, aryl, optionally substituted and R^7, R^8 and R^9 are each independently selected from H, alkyl, aryl, both optionally substituted.

Detailed description of the invention

Processes for preparing the concentrated detergent powder composition of the present invention are known in the art and various improvements thereof are described in the patent literature, e.g. EP-A-367,339 (Unilever) and EP-A-390,251 (Unilever).

The present invention is not concerned with these concentration and densifying production methods **per se**. The concentrated powder compositions of the invention can be obtained on the basis of any of the densifying and compacting methods known in the art; in such processes the bleach component including the catalyst is normally dry-mixed with the densified powder as one of the last steps of the manufacturing process.
The invention is of particular advantage to concentrated detergent powder compositions having a bulk density within the range of from 650 g/l to about 1200 g/l, preferably from 750 g/l to 1000 g/l.

The bleach catalyst

The manganese complexes which may be included in the detergent bleach composition of the present invention, are reported in EP-A-544,490. These complexes were found to be not only unusually effective but also remarkably storage stable bleach and oxidation catalysts. In the further description of the invention they will also be referred to as the "bleach catalyst"" or simply "catalyst".
The concentration of th bleach catalyst in the detergent

bleach composition f the invention is fr m 0.004 to 1.0%, preferably from 0.008 to 0.5% by weight.

Examples of suitable ligands in their simplest form which may be present in the bleach catalysts are:

(i) 1,4,7-triazacyclononane;
1,4,7-triazacyclodecane;
1,4,8-triazacycloundecane;
1,5,9-triazacyclododecane.
1,4,7-trimethyl-1,4,7-triazacyclononane.
1,4,7-trimethyl-1,4,7-triacyclodecane;
1,4,8-trimethyl-1,4,8-triazacycloundecane;
1,5,9-trimethyl-1,5,9-triazacyclododecane.

(ii) Tris(pyridin-2-yl)methane;
Tris(pyrazol-1-yl)methane;
Tris(imidazol-2-yl)methane;
Tris(Triazol-1-yl)methane.

(iii) Tris(pyridin-2-yl)borate;
Tris(triazol-1-yl)borate;
Tris(pyrazol-1-yl)borate;

Tris(imidazol-2-yl)phosphine;
Tris(imidazol-2-yl)borate.

(iv) 1,3,5-trisamino-cyclohexane;
1,1,1-tris(methylamino)ethane.

(v) Bis(pyridin-2-yl-methyl)amine;
Bis(pyrazol-1-yl-methyl)amine;
Bis(triazol-1-yl-methyl)amine;
Bis(imidazol-2-yl-methyl)amine,

These ligands which may be optionally substituted on the amine N-atom and/or the CH_2 carbon atom and/or the aromatic ring, are all c nnected to another ligand by a bridging unit as m ntion d in the definition of the inv ntion.

Bl ach catalysts containing thus connected ligands with different chemical structure, are within the scope of the invention.
Of these, the following ligand is especially preferred: 1,2-bis(4,7-dimethyl-1,4,7-triaza-1-cyclonoyl) ethane (Et-bridged(Me_2TACN)$_2$).

The type of counter-ion Y for charge neutrality is not critical for the activity of the complex and can be selected from for example any of the following counter-ions: chloride; sulphate; nitrate; methylsulphate; surfactant-anions, such as the long-chain alkylsulphates, alkylsulphonates, alkylbenzenesulphonates, tosylate; trifluormethylsulphonate; perchlorate (ClO_4^-), BF_4^- and PF_6^- , though some counter-ions are more preferred than others for reasons of product property and safety.

Having regard to its storage stability, the most preferred manganese complex as used in the present invention is:

$$[(\text{Et-bridged}(Me_2TACN)_2)Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)]^{2+}(PF_6^-)_2.$$

<u>The peroxy bleaching agent</u>
The level of peroxy bleaching agents in the detergent bleach compositions of the invention is in the range of from 5 to 35%, preferably from 10 to 25% by weight.

These peroxy bleaching agents may be compounds which are capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons.

Alkylhydroxy peroxides are another class of peroxy bleaching agents. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

Organic peroxyacids may also be suitable as the peroxy bleaching agent. Such materials normally have the general formula:

$$HOO-\overset{O}{\overset{\|}{C}}-R-Y$$

wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a pheylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or

$$\overset{O}{\overset{\|}{C}}-OOH$$

group or a quaternary ammonium group.

Typical monoperoxy acids useful herein include, for example:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-α-naphthoic acid;

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxylauric acid, peroxystearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and

(iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

(iv) 1,12-diperoxydodecanedioic acid (DPDA);

(v) 1,9-diperoxyazelaic acid;

(vi) diperoxybrassilic acid; diperoxysebasic acid and diperoxyisophthalic acid;

(vii) 2-decyldiperoxybutane-1,4-diotic acid; and

(viii) 4,4'-sulphonylbisperoxybenzoic acid.

Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10 % by weight, preferably from 4-8 % by weight.

All these peroxide compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor and/or an organic bleach catalyst not containing a transition metal.

Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and US Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US Patent 4,751,015 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:
2-(N,N,N-trimethyl ammonium) thyl sodium-4-sulphonphenyl carbonate chloride - (SPCC);
N-octyl,N,N-dimehyl-N_{10}-carbophenoxy decyl ammonium

chloride - (ODC);
3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and
N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification No.'s 458,396 and 464,880.

Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others.

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoloxy benzoate; SPCC; trimethyl ammonium toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyloxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

The precursors may be used in an amount of up to 12 %, preferably from 2-10 % by weight, of the composition.
As further improvement the composition may also additionally include an organic bleach catalyst of the sulfonimine type, as disclosed in EP-A-453,002 and EP-A-446,982.

<u>The surface-active material</u>

The detergent bleach compositions of the invention generally contain surface-active material in an amount of from 10 to 50% by weight. Said surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C_9-C_{10}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ester of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of higher (C_9-C_{18}) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane-monosulphonates such as those derived by racting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reaction paraffins with SO_2 and C_{12} and then hydrolysing with a base to produce a random sulphonate; s dium an ammonium C_7-C_{12} dialkyl sul-

phosccinates; and olefin sulphonates which term is used to describe material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralising and hydroysing the reaction product. The preferred anionic detergent compounds are sodium (C_{10}-C_{15}) alkylbenzene sulphonates, sodium C_{16}-C_{18}) alkyl ether sulphates.

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{22}) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulphoxides.

Amphoteric or zwitterionic surface-active compounds can also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and nonionic actives.

As disclosed by EP-A-544,490, the performance of the hereinbefore described bleach catalyst, may be dependent upon the active detergent system and the builder system present in the detergent bleach composition of the invention.

The d tergent bleach composition of the invention c mprises from 10 to 50% by weight of a surface active agent. Said

composition will preferably comprise from 1-15 % wt of anionic surfactant and from 10-40 % by weight of nonionic surfactant. In a further preferred embodiment the detergent active system is free from C_{16}-C_{12} fatty acids soaps.

The detergency builder

The detergent composition of the invention also contains a detergency builder in an amount of from about 15-80 % by weight, preferably from about 10-60 % by weight.

Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) caladium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as disclosed in US Patents 4,144,226 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also know as Zeolite P), zeolite C, zeolite X, zeolite Y and also the zeolite P type as described in EP-A-0384070.

In particular, the compositions of the invention may contain any on of the organic and inorganic builder materials, though, for environmental reasons, phosphate

builders are preferably omitted or only used in very small amounts.
Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyloxy malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder material, each of which can be used as the main builder, either alone or in admixture with other builders or polymers as co-builder.

It is preferred that the composition contains not more than 5% by weight of a carbonate builder, expressed as sodium carbonate, more preferable not more than 2.5 % by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

<u>The enzymes material</u>
Enzymes are preferably present in the composition of the invention in an amount ranging from 0.001 to 5% by weight, more preferably from 0.01 to 3% by weight, depending upon their activity.
The enzymes are generally incorporated in the form of granules, prills or "marumes". For proteolytic enzymes, the amount is such that the final detergent product has a proteolytic activity of about 2-20 Anson units per kilogram of final product.

The types of enzymes applied in the detergent composition of the invention may be proteolytic, amylolytic, cellulolytic, or lipolytic enzymes, or mixtures thereof. Preferred enzymes are proteolytic enzymes.

The proteolytic nzymes which are suitable for use in the present invention are catalytically active protein materials which degrade or alter protein types of stains

when present as in fabric stains, in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal or yeast origin. They comprise natural types of enzyme and genetically engineered variants.

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the composition of the invention. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of **B. subtilis** and **B. licheniformis**, such as the commercially available subtilisins Maxatase , as supplied by Gist-Brocades N.V. Delft, Holland, and Alcalase , as supplied by Novo Industri A/S, Copenhagen, Denmark.

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, and being commercially available, e.g. from Novo Industri A/S under the registered trade names Esperase and Savinase . The preparation of these and analogous enzymes is described in British Patent Specification 1,243,784. Other examples of suitable proteases are pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, papain, bromelin, carboxypeptidases A and B, aminopeptidase and aspergillopeptidases A and B.

<u>Other ingredients</u>

Apart from the components already mentioned, the detergent bleach compositions of the invention can contain any of the conventional additives in amounts of which such materials are normally employed in fabric washing detergent compositions. Examples of these additives include buffers such as carbonates, lath r boosters, such as alkanolamides, particularly the mon ethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants,

such as alkyl phosphates and silicones; anti-redeposition agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilizers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate, sodium silicate etc.; and usually in very small amounts, fluorescent agents; perfumes; germicides and colourants.

When using a hydrogenperoxide source, such as sodium perborate or sodium percarbonate, as the bleaching agent, it is preferred that the composition contains not more than 5 % by weight of a carbonate buffer, expressed as sodium carbonate, more preferable not more than 2.5% by weight to substantially nil, if the composition pH lies in the lower alkaline region of up to 10.

Of the additives, transition metal sequestrants, such as EDTA and the phosphonic acid derivatives, e.g. ethylene diamine tetra-(methylene phosphonate)-EDTMP- are of special importance, as not only do they improve the stability of the catalyst/H_2O_2 system and sensitive ingredients, such as enzymes, fluorescent agents, perfumes and the like, but also improve the bleach performance, especially at the higher pH region of above 10, particularly at pH 10.5 and above.

Accordingly detergent bleach compositions comprising a surface-active material, a peroxide bleaching agent, the manganese complex bleach catalyst, a carbonate builder and a transition metal sequestrant, having pH in solution of above 10, especially of 10.5 and above, are within the purview of the present invention.

Anoth r optional but highly desirable additive ingredient with multi-functional charact ristics in deterg nt com-

positions is from 0.1 % to about 3 % by weight of a polymeric material having a molecular weight of from 1,000 to 2,000,000 and which can be a homo- or co-polymer of acrylic acid, maleic acid, or salt or anhydride thereof, vinyl pyrrolidone, methyl- or ethylvinyl ethers, and other polymerizable vinyl monomers. Preferred examples of such polymeric materials are polyacrylic acid or plyacrylate; polymaleic acid/acrylic acid copolymer; 70-30 acrylic acid/hydroxyethyl maleate copolymer; 1:1 styrene/maleic acid copolymer; isobutylene/maleic acid and diisobutylene/maleic acid copolymers; methyl- and ethylvinylether/maleic acid copolymers; ethylene/maleic acid copolymer; polyvinyl pyrrolidone; and vinyl pyrrolidone/maleic acid copolymer.

<u>Experimental Storage Tests</u>

Storage experiments were carried out in open topped plastic cups containing approximately 5 g of bleaching detergent formulation. The vessels were stored at 37°C/70% RH (RH = relative humidity) for several periods.

<u>Experimental method</u>

The bleaching performance was determined of detergent products which had been stored during 0, 7, 14, and 42 days, using the above conditions.
Bleach experiments were carried out in glass vessels, equipped with a temperature controlled heating spiral in quartz, magnetic stirrer, thermo-couple and pH-electrode.

The experiments were carried out at an isothermal temperature of 60°C, whereby Millipore ultra pure water was used at a pH of 10. Furthermore, a dosage of approximately 5 g/l of the bleaching detergent formulation with catalyst to be tested was applied for each experiment. The test formulation had the following general composition:

component	parts by weight
base composition	62.26
sodium carbonate	4.00
sodium percarbonate	20.50
TAED	9.25
Dequest 2047	0.42
Minors, including fluorescer, anti-foaming agent, water	3.53
Manganese complex catalyst	0.04

2 tea-stained cotton test cloth (BC-1) were washed in 1 liter millipore ultra pure water at 60°C and containing 5 g/l of the detergent formulation with catalyst to be tested. During the test the pH was adjusted to 10.0. After 15 minutes, one cloth was removed from the solution, after 30 minutes the second was removed. The cloths are rinsed with tap water for 10 minutes and dried in a tumbler drier for 15 minutes.

After rinsing and drying the reflectance at 460 nm was measured. The difference in reflectance between the thus measured value and the (reference) value measured before the washing treatment,i.e. the ΔR value, is a measure for the bleach activity.

Furthermore, the H_2O_2-content (in mmol/l H_2O_2) was determined after washing periods of 15 respectively 30 minutes, using the following method.

To 20 ml 4N H_2SO_4 25 ml of the solution is added (in a 300 ml erlenmeyer flask). Add 20 ml 10% potassium iodide, 0.1 ml 20% ammonium heptamolybdate, 0.2 g sodium bicarbonate. Store the erlenmeyer flask in the dark for 3 minutes. Determine the amount of H_2O_2 by titrating with sodium thiosulphate (0.05 mol/l).

1 ml of the thiosulphate s lution equals 1 mmol/l H_2O_2.

The invention will now be illustrated by way of the following non-limiting examples.

Preparation Examples

Synthesis of 1,2-bis(4,7-dimethyl-1,4,7-triaza-1-cyclonoyl) ethane (Et-bridged(Me_2TACN)$_2$).

99.4 g distilled 1,4,7-triazacyclononane ((T.J. Atkins, et al, Org. Synth., 58, 86 (1978)) was warmed to 65 °C (without solvent) and 91.7g of N,N-dimethylformamide dimethyl acetal was added dropwise as fast as possible while stirring between 60 and 70 °C. The mixture was refluxed for 16 h, cooled and the low-boiling products were evaporated. The resulting tricyclo[5.2.1.0^{4,10}]-1,4,7-trazadecane (1) was purified by destillation under vacuum (bp 77 °C/1 mm).

1,2-dibromoethane (3.25 g) was added to (1) (6.0 g) in 30 ml acetonitrile and the mixture was kept at room temperature for 4 days. The precipitate obtained was filtered, washed with acetonitrile and ether and dried to leave 7.65 g of white microcrystalline salt (which is: 1,2-bis(tricyclo[5.2.1.0^{4,10}]-1,4,7-trazadecanyl)ethane dibromide (2)).

7.0 g of compound 2 was dissolved in 21 g of formic acid and 14 g of 37% formaldehyde was added. The mixture was heated at 95 °C for 24 h , then cooled and evaporated. Water was added and the solution was again evaporated. The remaining oil was dissolved in 100 ml water and the impurities were extracted by washing with ether. The water layer was made pH>12 by addition of 40% NaOH solution and then 5 times extracted with hexane. Drying and evaporation of ether, yielded 5.0 g of an almost colourless oil, which was further purified by vacuum destillation (bp 195 °C/1 mm) (3).

Synth sis of Mn c mplex: $[(\text{Et-bridged}(Me_2TACN)_2)Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)]^{2+}(PF_6^-)_2$.

2.5 gr of ligand (3) was dissolved in 100 ml ethanol/water (2/1 v/v) and 3.7 g of $Mn(OAc)_2.4H_2O$ and 4.14 g of KPF_6 were added. The mixture was stirred for 20 minutes at 40-55°C, and subsequentyl cooled (ice bath) whilst stirring. After 10 minutes a freshly permixed solution containing 1 ml, 1M of H_2O_2 and 1 ml of 1.5 M NaOH was added dropwise during 3-5 minutes. After stirring for another 10-15 minutes at 0°C, the mixture was neutralised with 2 M H_3CCOOH to pH 7, the celite was added and the mixture was filtered over a bed of celite. The combined filtrates were evaporated (vacuum, 40°C) and the product was dissolved in acetonitrile to remive salts and again filtered. The filtrate was partially evaporated (vacuum , 40°C), water was added and filtered. The solid was washed with ethanol and hexane and dried. Further purification took place by dissolving 4.0 g of the green powder in 30 ml of acetonitrile and allowing ether to diffuse in the solution at 5 °C. Green-black crystals (3.8 g) were isolated.

Example 1, Comparative Example A

Two detergent products having the general composition shown above and including different types of manganese complex catalyst were first stored during several periods (0, 7, 14, and 42 days) whereby the conditions as described above were applied. Subsequently, these detergent products were tested using the above described experimental method.

The tested products include the following base composition:

base composition	parts by weight
Na-PAS 1)	9.30
Nonionic 7EO 2)	5.95
Nonionic 3EO 3)	3.97
Soap	1.54
Zeolite A24 (anhydrous)	31.27
light soda ash	2.83
Moisture, salts, NDOM, minors	7.40

wherein:

1) Na-PAS : C_{12} sodium salt of primary alkyl sulphate;

2) Nonionic 7EO : C_{12}-C_{14} ethoxylated alcohol having on average 7 ethylene oxide groups (e.g. Synperonic A7, ex ICI);

3) Nonionic 3EO : C_{12}-C_{14} ethoxylated alcohol having on average 3 ethylene oxide groups (e.g. Synperonic A3, ex ICI).

The following manganese complex catalysts were present in the products to be tested:

Example no	Mn complex catalyst type
A	$[Mn^{IV}_2(\mu\text{-}O)_3(Me_3TACN)_2]^{2+}(PF_6^-)_2.H_2O$
1	$[(Et\text{-}bridged(Me_2TACN)_2Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)]^{2+}(PF_6^-)_2$

The following results were obtained, showing ΔR values found after washing BC-1 test cloth during 15 respectively 30 minutes with the detergent products to be tested, whereby said detergent products had previously been stored during the indicated periods of time.

Example no.	A		1	
	15'	30'	15'	30'
Storage periods (days)				
0	32	32	25	30
7	30	31	21	29
14	26	29	24	29
42	16	19	20	25

From these results it can be derived that the reduction in bleaching activity of the product according to the present invention is significantly less than the reduction observed for the product of Example A , when comparing the respective ΔR values found for the products stored for 42 days with those for the products not stored at all.

Furthermore, the following H_2O_2-contents were found after washing BC-1 test cloth during 15 respectively 30 minutes with the detergent products as indicated.

Example no.	A		1	
	15'	30'	15'	30'
Storage period (days)				
0	2.23	1.60	8.29	7.30
7	2.92	2.20	8.39	7.18
14	3.01	2.22	7.93	6.83
42	8.19	7.83	8.63	7.25

From these results, it can be concluded that the product of the prior art (Example A) gives much more H_2O_2 decomposition than the product of the present invention, after a storage period of up to about 2 weeks. It can also be seen that the H_2O_2 decomposition resulting from washing with the product of the present invention does not clearly reduce when longer storage peri ds are applied.

CLAIMS

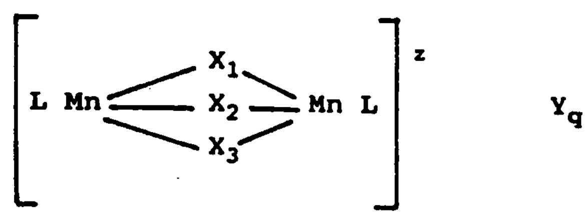
1. A concentrated detergent powder composition having a bulk density of above 600 g/l, comprising:

(a) from 10 to 50% by weight of a surface active material;

(b) from 15 to 80% by weight of a detergency builder or builder mixture;

(c) from 5 to 35% by weight of a peroxy bleaching agent; and

(d) from 0.004 to 1.0 by weight of a bleach catalyst, characterised in that said bleach catalyst is a dinuclear manganese complex having the formula:



wherein Mn is manganese which can individually be in the III or IV oxidation state; X_1, X_2 and X_3 each independently represent a coordinating or bridging species selected from the group consisting of H_2O, O_2^{2-}, O^{2-}, OH^-, HO_2^-, SH^-, S^{2-}, $>SO$, Cl^-, N_3^-, SCN^-, $RCOO^-$, RSO^-_3, RBO_2^{2-}, NH_2^- and NR_3, with R being H, alkyl, aryl, both optionally substituted, $R'COO^-$ where R' is alkyl, aryl, both optionally substituted;

L is a ligand which is an organic molecule containing at least three nitrogen atoms which coordinates via all or some of the nitrogen atoms to the manganese centres;

z denotes the charge of the complex and is an integer which can be positive or negative;

Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the charge z of the complex;

and q = z/[charge Y]

whereby th bleach catalyst comprises two ligands L having the formula:

$$\left[NR^3 - (CR^1(R^2))_t \right]_s$$

wherein t is an integer from 2 to 3;
s is an integer from 3 to 4;
R^1 and R^2 are each independently selected from H, alkyl, aryl, both optionally substituted; and
R^3 is independently selected from hydrogen, alkyl, aryl both optionally substituted, with the proviso that a bridging unit R^4 is formed by one R^3 unit from each ligand where R^4 is the group $C_nR^5R^6-(D)_p-C_mR^5R^6$ where p is zero or one;
D is selected from a heteroatom or a heteroatom containing group, such as oxygen and NR^7, or is part of an aromatic or saturated homonuclear or heteronuclear ring;
n is an integer from 1 to 4;
m is an integer from 1 to 4;
with the proviso that $n + m \leq 4$;
R^5 and R^6 are each independently selected from H, NR^8 and OR^9, alkyl, aryl, optionally substituted and R^7, R^8 and R^9 are each independently selected from H, alkyl, aryl, both optionally substituted.

2. A composition according to claim 1, wherein it comprises from 0.008 to 0.5% by weight of the bleach catalyst.

3. A composition according to claim 1 or 2, wherein it has a bulk density of from 650 g/l to about 1200 g/l.

4. A composition according to any of claims 1-3, wherein the bleach catalyst is:
$[(\text{Et-bridged}(Me_2TACN)_2)Mn^{III}Mn^{IV}(\mu\text{-}O)_2(\mu\text{-}OAc)]^{2+}(PF_6^-)_2$